Summer 2005

Laser Depletion Grating Study of the Photodissociation of Chlorine Dioxide (OClO)

Katherine Coens

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Summer Science 2005 at Kenyon College

Katherine Coens, James Keller, Department of Chemistry

Abstract

This summer, I attempted to use laser depletion grating spectroscopy techniques as a method to study the effects that various vibrational states have on the decomposition of OClO (chlorine dioxide). Many different problems were encountered during this project, mostly with the Nd:YAG laser. These problems included insufficient power levels, misaligned optics, a "black slime mold," and finally, and most detrimentally, leaks in the cooling system.

Experimental

OClO Generation

$$KClO_4 + C_2H_2O_4 + H_2SO_4 \rightarrow OClO + 2CO_2 + KSO_4$$

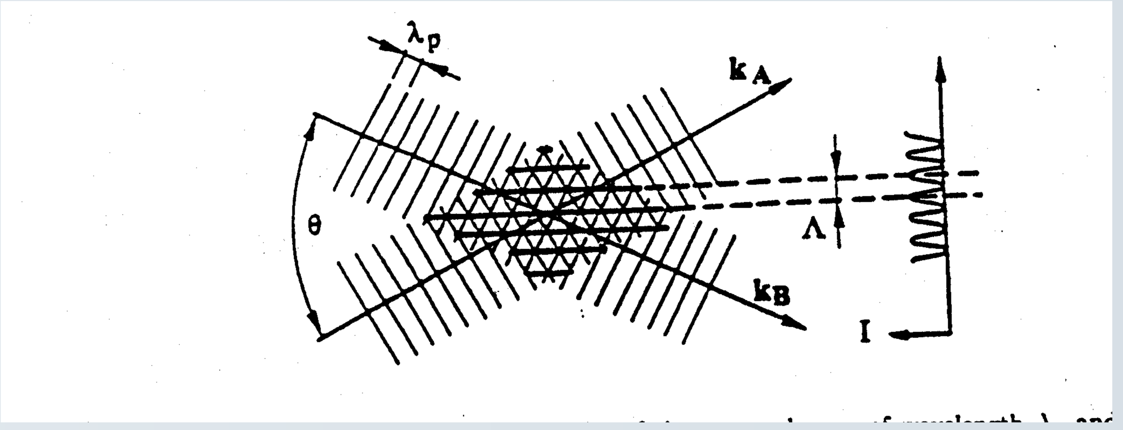
OClO Photodissociation

(I) $OClO \rightarrow OCl + O$

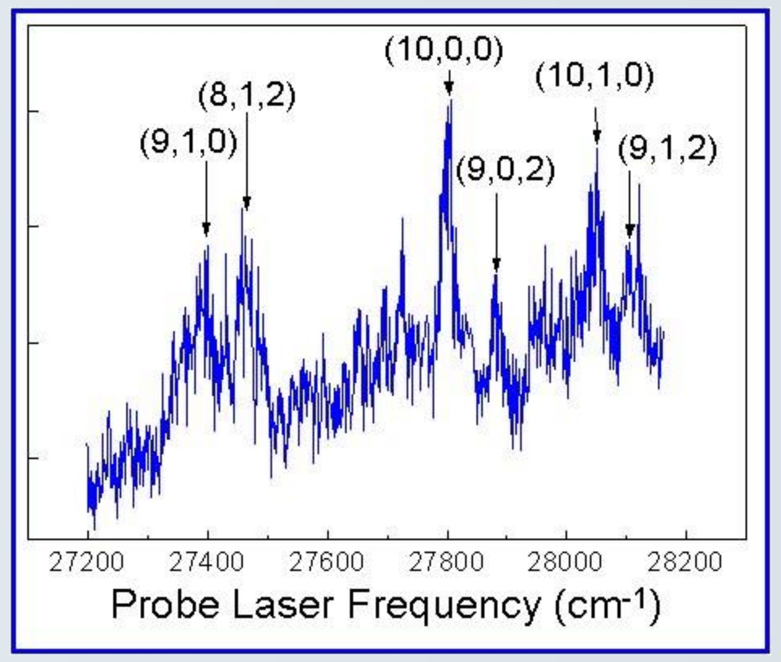
(II) $OClO \rightarrow Cl + O_2$

OClO Generator

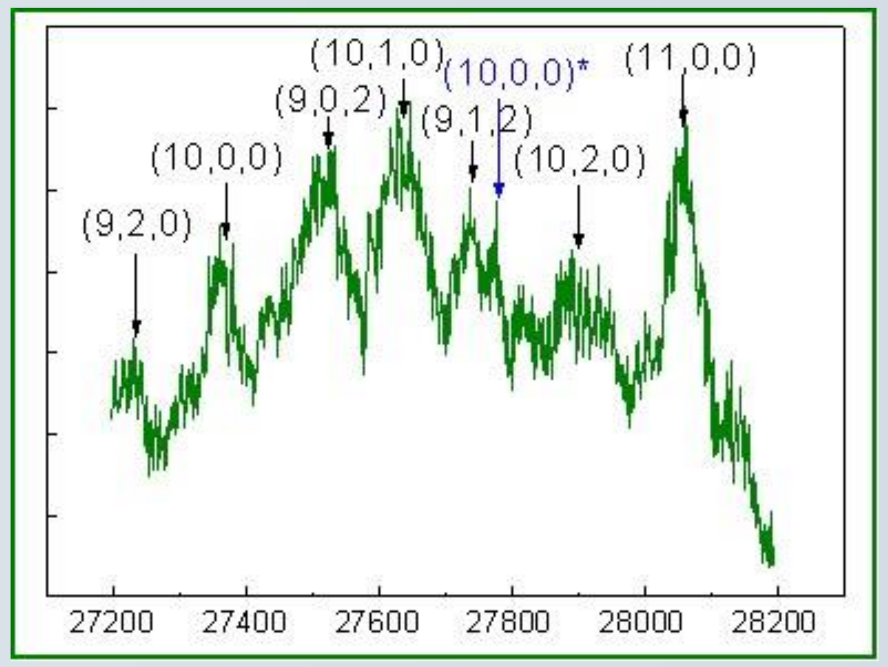
Laser Depletion Grating



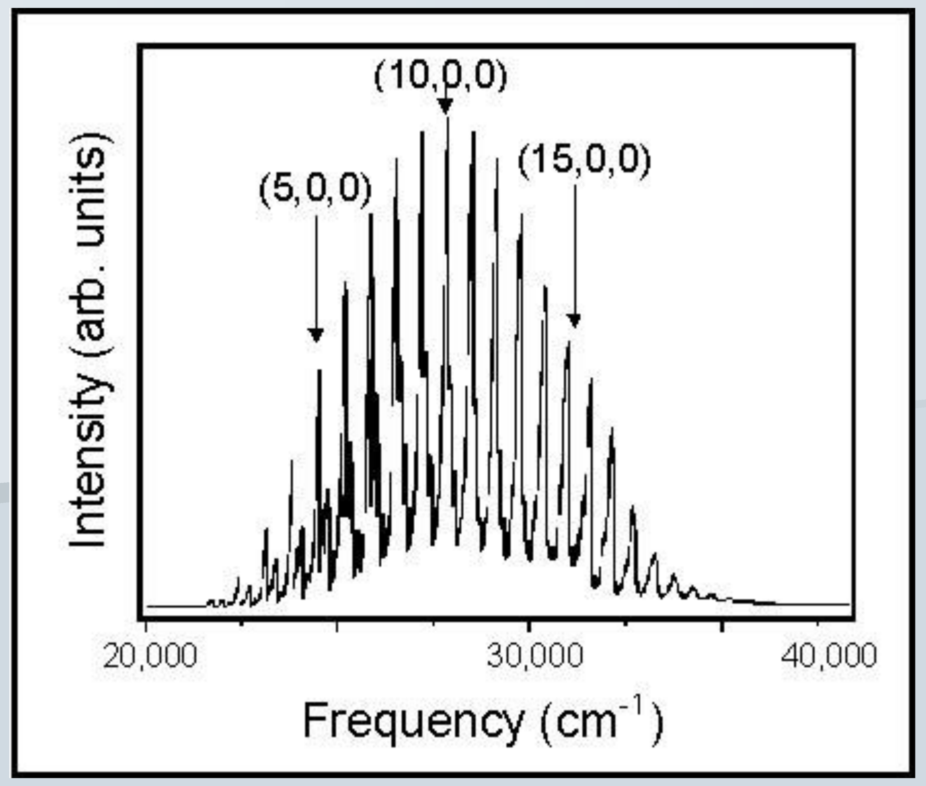
OClO Cold Spectrum



OClO Hot Spectrum



Absorption Spectrum



Results and Discussion

This summer, we hoped to study how the initial state vibrations of OClO affect how it dissociates in the excited state. We focused on the (10, 0, 0) vibration because it has 10 quanta of symmetric stretch and no bending energy. Notice in the absorption spectrum, this is the highest peak, so it excites readily. In this system, some of the molecules have small vibrational energies, while others remain in the ground state. If the ground state molecules are excited, it produces a cold spectrum, if the vibrationally excited molecules are further excited, it produces the hot spectrum. Observation shows that the peaks in the hot spectrum are broader than the cold, as the molecule absorbs the energy more readily. By tuning each laser, we can selectively pick which vibrational states are excited and see how the spectra change.

There are no actual results to discuss in this project, as the laser never produced the power levels needed to proceed with the spectroscopy. Instead, we cleared up many of the background problems in the laser. The dyes are fresh, the black slime is gone, and the heat exchanger has been replaced. Hopefully, whoever continues the project will find the laser running a little better.

Future Directions

Now that the replacement heat exchanger has arrived, the power levels should be higher, giving stronger initial beams and better signal. Therefore, data collection on OClO could theoretically begin soon.

References

Crim, F. F. "Vibrationally Mediated Photodissociation: Exploring Excited-State Surfaces and Controlling Decomposition Pathways." *Annual Review of Physical Chemistry.* 1993. 44: 397-428.

Davis, H Floyd. Yuan T. Lee. " Photodissociation dynamics of OClO" *Journal of Chemical Physical Chemistry.* 105 (18) * November 1996. pp 8142-8163.

Esposito, Anthony P, Catherine E Foster, Robert A Beckman, Philip J Reid*. "Excited-State Dynamics of Chlorine Dioxide in the Condensed Phase from Resonance Raman Intensities." Journal of Physical Chemistry A 1997, 101, 5309-5319.

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